Equilibrium: Solid-Liquid

A given homogeneous liquid system comprises two chemical substances i and j at known T and p. The temperature and/or pressure are changed. Consequently chemical substance j spontaneously separates out as a solid phase but substance i does not. Hence the liquid becomes richer in chemical substance i.

The starting point of the analysis is the following equation for the affinity for spontaneous transfer of substance j from phase II to phase I [1].

\[
\delta \left( \frac{A_j}{T} \right) = \frac{[\Delta_{\text{trans}} H_j^0(T, p)]}{T^2} \cdot \delta T - \frac{[\Delta_{\text{trans}} V_j^0(T, p)]}{T} \cdot \delta p + R \cdot \delta \ln \left[ \frac{x_j(\text{I}) \cdot f_j(\text{I})}{x_j(\text{II}) \cdot f_j(\text{II})} \right]
\]

(a)

For two equilibrium states such that \( \delta (A_j/T) \) is zero for the transfer of chemical substance j from phase II to phase I,

\[
R \cdot \delta \ln \left[ \frac{x_j(\text{II}) \cdot f_j(\text{II})}{x_j(\text{I}) \cdot f_j(\text{I})} \right] = \frac{[\Delta_{\text{trans}} H_j^0(T, p)]}{T^2} \cdot \delta T - \frac{[\Delta_{\text{trans}} V_j^0(T, p)]}{T} \cdot \delta p
\]

(b)

In this application, chemical substance i cannot exist in phase I. Then the equilibrium states are determined by substance j. Further we consider the case where state I corresponds to pure j such that \( x_j(\text{I}) \cdot f_j(\text{I}) \) is unity at reference temperature \( T_{\text{ref}} \) and reference pressure \( p_{\text{ref}} \). We integrate equation (b) between these two states.

\[
\ln[x_j(\text{II}) \cdot f_j(\text{II})] = \int_{T_{\text{ref}}}^{T} \frac{[\Delta_{\text{trans}} H_j^0(T, p)]}{R \cdot T^2} \cdot \text{dT} - \int_{p_{\text{ref}}}^{p} \frac{[\Delta_{\text{trans}} V_j^0(T, p)]}{R \cdot T} \cdot \text{dp}
\]

(c)

In the event that the pressure is constant,

\[
\ln[x_j(\text{II}) \cdot f_j(\text{II})] = \int_{T_{\text{ref}}}^{T} \frac{[\Delta_{\text{trans}} H_j^0(T, p)]}{R \cdot T^2} \cdot \text{dT}
\]

(d)

Footnote

[1] By definition, for the transfer of one mole of chemical substance j from phase II to phase I, \( A_j = -[\mu_j(\text{I}) - \mu_j(\text{II})] \); Or, \( A_j = \mu_j(\text{II}) - \mu_j(\text{I}) \)